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Molecular Weight–Viscosity Relationship of Gamma-Irradiated Octadecyl Vinyl Ether and Octadecyl Methacrylate

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It is well known[1] that gamma radiation may be used to initiate addition-type polymerizations. Irradiation polymerization of certain monomer systems can be successfully carried out in the solid state,[2] yielding molecular structures that differ from those obtained by the conventional initiators. Recently it has been shown[3] that the rate of polymerization and the intrinsic viscosity of vinyl stearate as a function of the temperature of polymerization pass through a discontinuity at approximately the melting point of the monomer. In the present work, we studied the effect of the quantity of gamma radiation on the molecular weight of the homo-polymers produced when octadecyl vinyl ether and octadecyl methacrylate were irradiated at above and below their melting points. The molecular weight-viscosity relationship was determined for these polymers.

Octadecyl vinyl ether, prepared by the method of Craig,[4] was obtained from General Aniline and Film Corporation* and was used without further purification. Octadecyl methacrylate was obtained from commercial material (Rohm and Haas Company*). The inhibitor present in the commercial product was removed by extraction with 25% Na_2CO_3 containing 1% NaOH; the monomer was then freed of alkali by successive washes with dilute HCl and water and was dried over $CaSO_4$. The crude monomer was recrystallized from five parts of acetone at 0°C. Octadecyl methacrylate having a saponification number of 166.7 (calculated, 165.8) and n_D^{50} of 1.4399 was thus obtained in 41% yield. Ampules were filled with approximately 18 grams of monomer, evacuated to 10^{-2} mm., and sealed. The octadecyl vinyl ether and octadecyl methacrylate monomers were subjected to gamma radiation from a cobalt-60 source at Brookhaven National Laboratory. Exposures to field intensities which gave 0.3 to 5.0 megarep were used in irradiating the octadecyl methacrylate at −10

* Reference to commercial products in this paper is not intended to be a recommendation of these products by the United States Department of Agriculture over others not mentioned.

and +30°C. (below and above 17°C., the melting point of the monomer). Octadecyl vinyl ether was exposed to field intensities yielding 0.5 to 10 megarep at temperatures of 10 and 50°C. (below and above 28°C., the melting point of the monomer). The yields were calculated from the refractive index found and the refractive indices of the monomer and polymer, a linear relationship being assumed to hold between per cent composition of the monomer-polymer mixture and the refractive index. The samples of polymer were isolated by dissolving the mixture of polymer and monomer in three volumes of benzene per gram of polymer and monomer and precipitating the polymer in three volumes of methanol per volume of benzene solution. This process was repeated. The polymers were then filtered off and dried at room temperature. Two samples of poly (octadecyl vinyl ether) were prepared by ionic initiation for comparison with the radiation initiated polymers. Sample 3 (Table I) was polymerized in Skellysolve F* by initiation with boron trifluoride in ether at 60°C. and Sample 7 was polymerized in toluene at 0°C. in the presence of the same catalyst. After the polymers had been isolated by pouring their solutions into acetone and methanol, respectively, both samples were redissolved in ether and precipitated in acetone.

TABLE I

Molecular Weight and Solution Characteristics of Poly(octadecyl methacrylate) and Poly(octadecyl vinyl ether)

Sample	Radiation, megarep	Temperature, °C.	Conversion, %	Molecular weight, M	Radius of gyration, R_p, A.	$[\eta]$, dl./g.	k'
			Poly(octadecyl methacrylate)				
1	0.3	30	73	1,667,000	500	1.147	0.323
2	1.0	30	83	1,650,000[a]		1.008	0.343
3	0.3	−10	57	988,000	580	0.828	0.321
4	5.0	30	85	820,000[a]		0.638	0.415
5	3.0	−10	99	789,000	560	0.530	0.391
6	1.0	−10	79	405,000[a]		0.373	0.410
7	5.0	−10	85	231,600	330	0.262	0.518
			Poly(octadecyl vinyl ether)				
1	0.5	10	15	107,000		0.132	0.534
2	2	10	7.6	64,900		0.103	0.472
3	Ionic polymerization	60	100	50,000		0.101	0.882
4	5	10	85	42,000		0.090	0.617
5	2	50	13	11,000[a]		0.059	0
6	10	50	60	9,400		0.056	0
7	Ionic polymerization	0	100	5,500[a]		0.046	2.38

[a] Obtained by interpolation from plot of log $[\eta]$ vs. log M.

In preparation for the solution studies, all the polymer samples were dissolved in tetrahydrofuran at concentrations ranging from 0.05 to 8.8% for poly(octadecyl vinyl ether) and from 0.05 to 2.0% for poly(octadecyl methacrylate). The solutions were clarified by pressure filtration through ultrafine-porosity, sintered glass filters.

Light scattering measurements, at angles from 135 to 35° to the primary beam, were made with a Brice-Phoenix photometer with the use of a cylindrical scattering cell[5] at a wavelength of 546 mμ. The refractive increments were determined in a direct reading differential refractometer[6]; the average dn/dc for poly (octadecyl vinyl ether) was 0.0674, and that for poly(octadecyl methacrylate) was 0.0855 at λ546 for the concentration ranges previously mentioned. The intrinsic viscosities given were deduced from measurements on an Ostwald-type viscometer at 30°C.

Table I shows the results of the light scattering and viscosity determinations along with the calculated radii of gyration, R_p, and k' values. The molecular weights observed for poly(octadecyl methacrylate) ranged from 231,600 to 1,667,000 and the viscosities ranged from 0.26 dl./g. to 1.147 dl./g. The radii of gyration (calculated from plot of Hc/τ versus $\sin^2(\theta/2)$ at zero concentration)[7] ranged from 330 to 580A. The sample with the highest molecular weight did not exhibit the largest radius of gyration. The k' values, obtained from the Huggins equation,[8] ranged from 0.321 to 0.518, generally increasing as viscosity decreased. The sample of highest molecular weight was prepared at high (30°C.) temperature with low radiation exposure (0.3 megarep). However, the samples prepared at −10°C. and 0.3 megarep exhibited larger radii of gyration, thus indicating that the polymer sample prepared at 30°C. was probably more highly branched. The samples of poly(octadecyl vinyl ether) ranged in molecular weight from 5500 to 107,000, while intrinsic viscosity and k' values ranged from 0.046 to 0.132 and from 0 to 2.38, respectively. No radii of gyration could be calculated due to the low molecular weight (small particle size) of the polymer. The sample of highest molecular weight was prepared at low temperature (10°C.) and low radiation exposure (0.5 megarep), while the sample prepared at 50°C. and 10 megarep gave the lowest molecular weight for the irradiated samples. For Samples 3 and 7, which were prepared by ionic polymerization, the high temperature (60°C.) reaction yielded the higher molecular weight polymer. This polymer, however, had only half the molecular weight of Sample 1, which was prepared at 10°C. and 0.5 megarep radiation exposure.

The relationship between viscosity and molecular weight of a polymer system can be described by the general formula $[\eta] = K'M^a$, where K' and a are constants determined by the intercept and slope, respectively, of a plot of log $[\eta]$ versus log M. Figures 1 and 2 show such plots for poly(octadecyl methacrylate) and poly(octadecyl vinyl ether). The values obtained for K' and a are shown in Table II along with comparable values reported in the literature. For poly(octadecyl methacrylate), K' was 0.25×10^{-4} and a was 0.75. Corresponding values reported for poly-

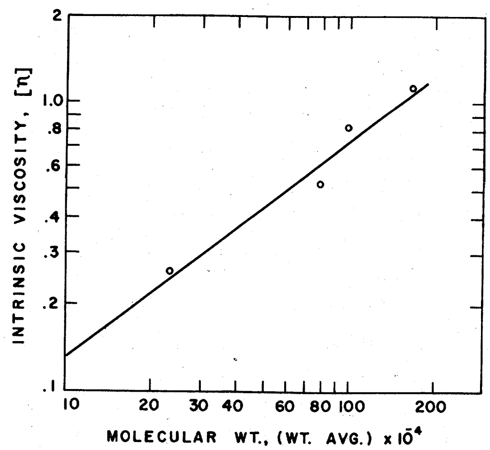

Fig. 1. Intrinsic viscosity-molecular weight relationship of octadecyl methacrylate polymers prepared by irradiation of monomer.

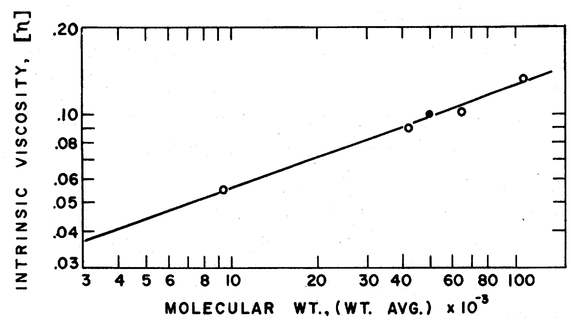

Fig. 2. Intrinsic viscosity-molecular weight relationship of vinyl octadecyl ether polymers: (O) prepared by irradiation of monomer; (●) prepared by ionic initiation.

TABLE II

Comparison of K' and a Values for Polymers Prepared by Irradiation with Those for Similar Polymers Prepared by Other Means

Sample	Solvent	Temperature, °C.	Molecular weight range	$K' \times 10^4$	a
Poly(octadecyl methacrylate)	Tetrahydrofuran	30	231,600–1,667,000	0.25	0.75
Poly(methyl methacrylate)[9]	Benzene	25	—	0.57	0.76
Poly(octadecyl vinyl ether)	Tetrahydrofuran	30	9,400–107,000	22.4	0.35
Poly(octadecyl vinyl ether)[10]	Cyclohexane[a] Benzene[b]	25	1300–15,000	17.0	0.47

[a] Molecular weight determination.
[b] Viscosity determination.

methyl methacrylate[9] were $K' = 0.57 \times 10^{-4}$ and $a = 0.76$. According to Flory,[9] a does not fall below 0.50 and rarely exceeds 0.80. However, for poly(octadecyl vinyl ether), a value of 0.35 was obtained for a. The corresponding value for poly(octadecyl vinyl ether) according to Gast[10] et al. was 0.47. The K' value presently obtained was 22.4×10^{-4}, compared to 17.0×10^{-4} reported by Gast et al.[10]

The highest molecular weights obtained for both poly(octadecyl methacrylate) and poly(octadecyl vinyl ether) were produced by the lowest radiation exposures. Greater exposure to radiation probably promoted chain scission leading to lower molecular weights. The two compounds were markedly different, in that the highest molecular weight for poly(octadecyl methacrylate) was obtained by irradiating in the molten state, while for poly(octadecyl vinyl ether), irradiating the solid monomer produced the highest molecular weight. However, the poly(octadecyl vinyl ether) sample prepared by ionic initiation gave a higher molecular weight when prepared above the melting temperature of the monomer. The highest molecular weight sample produced by irradiation was twice that of the highest molecular weight sample obtained by ionic polymerization.

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Synopsis

Octadecyl vinyl ether and octadecyl methacrylate monomer were polymerized by means of gamma radiation from a cobalt-60 source. The weight-average molecular weight and the intrinsic viscosity of the resulting polymers were determined. The constants K' and a were 0.25×10^{-4} and 0.75, respectively, for poly(octadecyl methacrylate) and 22.4×10^{-4} and 0.35, respectively, for poly(octadecyl vinyl ether).

Résumé

L'éther octadécyle-vinylique et le méthacrylate d'octadécyle ont été polymérisés par des radiations gamma provenant d'une source de cobalt 60. Le poids moléculaire moyen en poids et la viscosité intrinsèque de ces polymères sont déterminés. Les constantes K' et a étaient $0{,}25 \times 10^{-4}$ et 0,75, respectivement pour le polyméthacrylate d'octadécyle et 22.4×10^{-4} et 0,35, respectivement pour la polyéther octadécyle-vinylique.

Zusammenfassung

Monomerer Octadecylvinyläther und monomeres Octadecylmethacrylat wurden mittels der Gammastrahlung einer Kobalt-60-Quelle polymerisiert. Der Gewichtsmittelwert des Molekulargewichts und die Viskositätszahl der erhaltenen Polymeren wurden bestimmt. Die Konstanten K' und a ergaben sich zu $0{,}25 \times 10^{-4}$ und 0,75 für Poly-(octadecylmethacrylat), bzw. zu $22{,}4 \times 10^{-4}$ und 0,35 für Poly-(octadecylvinyläther).

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